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SOLIDIFICATION OF RADIOACTIVE INCINERATOR ASH - PART 2

Report No 91-188-K

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ABSTRACT

Immobilization of radioactive incinerator ash will likely be required to retard the release of radioactivity and toxic waste constituents into the ground water during its eventual disposal and to minimize the risk of ash dispersal during transportation. Part 1 considered the suitability of cement, water extendible polyester, polyethylene and asphalt as binders. Based on considerations of ash loading and leaching characteristics, asphalt appeared to be the favoured choice; however, high cadmium releases were observed from asphalted baghouse ash leachates. In Part 2, solidification in sulfur cement was investigated as well as properties of compacted waste forms. Sulfur cement waste forms incorporate less ash than asphalt and retard cadmium to a similar extent. Compaction offers a volume reduction factor significantly higher than that achieved with asphalt. Properties of compacts prepared from ash wetted using water, sodium hydroxide and sodium silicate solutions were investigated. A concept for compacting mixed bottom and baghouse ashes is described.

job	file	date	report no.
32-147-462	837.83	October 24, 1991	91-188-K

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A. Husain and D.Beaudry
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EXECUTIVE SUMMARY

Low-level combustible wastes such as rags, paper wipers, packings, coveralls etc, comprise approximately 70% of the solid radioactive wastes generated annually at Ontario Hydro nuclear generating stations. To reduce storage requirements, the wastes are burnt in the radioactive waste incinerator at BNPDS; an average gross volume reduction factor of 60:1 is typically obtained. Incineration is limited to waste packages having a maximum contact field of 60 mR/h; the majority of waste packages, however, have fields of less than 5 mR/h.

Batch pyrolysis in the primary chamber of the incinerator is performed at 500 deg.C while the afterburner is maintained at 950 deg.C. Each 15 m^3 burn produces about 0.25 m^3 of bottom ash (BA) and 0.015 m^3 baghouse ash (BHA). The ash is discharged into galvanized steel containers which are stored in concrete trenches or in the Low Level Storage Buildings at BNPDS.

Characterization studies performed earlier have indicated that the radioactivity in the ash is principally due to Co-60, La-140, Zr/Nb-95, Cs-137 and Cs-134. Based on their activities, the ash according to the US waste classification criteria constitutes Class A type waste and as such would not require immobilization. However, in addition to the radioactive contaminants present, the ash also contains low concentrations of hazardous heavy metal and organic (eg. dioxins and furans) constituents. Immobilization of the ash is thus required to retard the release of toxic waste constituents into the ground water during disposal. Immobilization would also minimize the risk of ash dispersal during transportation to the disposal site.

Several methods for ash immobilization have been reported in the literature. The suitability of cement, water extendible polyester resin (WEP), polyethylene (PE) and asphalt for immobilizing Ontario Hydro's incinerator ashes were investigated and previously reported. Investigations using sulfur cement and an assessment of compaction are presented in this report.

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Ash loadings in cement, WEP (BHA solidification was not feasible in this matrix), PE and asphalt were respectively, 42-51 wt % (loading depended on whether the cement paste was pelletized or not) 59, 40 and 67 wt %. Immobilization of the ashes in a pelletized cement waste form, asphalt or WEP resulted in an overall volume decrease while an overall increase in volume occurred in the other cases. Bottom ashes were satisfactorily immobilized in all matrices, i.e., compressive strengths and leach indices (of Cs-137) in all cases exceeded 10 CFR Part 61 requirements (60 psi and an index of 6, respectively). However, material interactions in the case of BHA limited the choice to PE, asphalt and cement with the latter requiring pelletization. In addition to the release of radioactivity, the release of heavy metals, cadmium, lead and silver into the leachants was also assessed. Bottom ash leachates from the asphalt matrix had undetectable concentrations of the heavy metals and thus asphalt appears to be a suitable matrix overall for BA immobilization. However, the leachates from asphalt samples containing BHA had cadmium concentrations in excess of the Regulation 309 release limit of 500 ppb. This aspect requires further assessment.

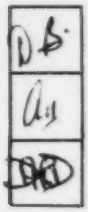
Ash loadings achieved in sulfur cement were < 40 wt % which is significantly lower compared to that obtained using asphalt. Compressive strength of sulfur cement waste forms exceeded 1000 psi. While sulfur cement offers some improvement over asphalt with respect to the leach index of Cs-134/137 and concentration of cadmium in the leachate, the cadmium toxicity still exceeded the regulatory limit.

In contrast to the various solidification matrices, compaction offers sustantially higher ash loadings (> 1.5 g/ml). Surprisingly, compacts of BA wetted with water, sodium silicate or sodium hydroxide exhibited compressive strengths comparable to and leach indices better than cement (unpelletized) waste forms. Also, the cadmium toxicity in the leachate from the BA compacts does not appear to be a concern. Baghouse ash compacts on the other hand did not have adequate post-immersion compressive strength and not surprisingly their leachates contain very high levels of cadmium.

Based on the foregoing and the likelihood of a super-compactor acquisition, compaction of mixed bottom and baghouse ashes is proposed for managing the incinerator ashes. The addition of a suitable wetting agent will minimize the potential for future hydrogen gas generation and avoid dust production during supercompaction. The compacts would be stored in an overpack with the space between the compacts and the overpack drum backfilled with sulfur cement, asphalt, WEP or cement. Backfilling in the overpack drum will provide an additional barrier to retard the migration of Cs and toxic metal constituents. Backfilling will reduce the overall ash loading from 1.6 g/ml to about 1.4 g/ml. Further work is required to fully develop the compaction option.

With the expected acquisition of a super-compactor in the near future, there is no incentive at present to further develop the solidification option using asphalt. However, should plans for acquiring the supercompactor alter or unforseen difficulties arise with implementing ash

compaction, asphalt could then be explored further. As with the compaction option, the BHA will need to be blended with BA to minimise cadmium toxicity in the leachate. Unlike compaction, material handling requirements during asphalt-ash blending will probably necessitate screening of the ash and hence separate conditioning of the screened and unscreened ash.



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SOLIDIFICATION OF RADIOACTIVE INCINERATOR ASH - PART 2

1.0 INTRODUCTION AND BACKGROUND

Low-level combustible wastes such as rags, paper wipers, packings, coveralls etc, comprise approximately 70% of the solid radioactive wastes generated annually at Ontario Hydro nuclear generating stations. To reduce storage requirements, the wastes are burnt in the radioactive waste incinerator at BNPDS; an average gross volume reduction factor of 60:1 is typically obtained. Incineration is limited to waste packages having a maximum contact field of 60 mR/h; the majority of waste packages, however, have fields of less than 5 mR/h.

Batch pyrolysis is performed at 500 °C in the primary chamber while the afterburner is maintained at 950 °C. Each 15 m^3 burn produces about 0.25 m^3 of bottom ash (BA) and 0.015 m^3 baghouse ash (BHA). The ash is discharged into galvanized steel containers which are stored in concrete trenches or in the Low Level Storage Buildings at the Waste Management Site.

Characterization studies/1-4/ have indicated that the radioactivity in the ash is principally due to Co-60, La-140, Zr/Nb-95, Cs-137 and Cs-134. Based on their activities, the ash according to the US waste classification criteria/5/ constitutes Class A type waste and as such would not require immobilization. However, in addition to the radioactive contaminants present, the ash also contains low concentrations of hazardous heavy metal and organic (eg., dioxins and furans) constituents. Immobilization of the ash is thus required to retard the release of toxic waste constituents into the ground water during disposal. Immobilization would also minimize the risk of ash dispersal during transportation to the disposal site.

Several methods for ash immobilization have been reported in the literature. Of these, the suitability of cement, bitumen, polyester resin (WEP) and polyethylene (PE) for immobilizing Ontario Hydro's ashes were investigated in Part 1 /6/. Optimal formulations were developed for each matrix. Samples with optimal ash loadings were then leached and

were developed for each matrix. Samples with optimal ash loadings were then leached and compression tested. Bottom ashes were satisfactorily immobilized in all matrices. However, material interactions in the case of BHA limited the choice to PE, asphalt and cement with the latter requiring pelletization. Based on considerations of ash loading and leaching characteristics of Cs-137, solidification in asphalt appeared to be the favoured choice for both types of ashes. However, high cadmium releases observed in leachates from asphalted BHA samples are of concern and require further assessment.

This report examines the suitability of modified sulfur cement as a solidification matrix and assesses compaction techniques for producing ash waste forms; both bottom and baghouse ashes were investigated. Results obtained are compared with those obtained earlier; based on this comparison, a concept for managing the ashes is outlined. Further work in support of this concept is in progress and will be reported in Part 3.

Modified sulfur cement is a thermoplastic material which has been extensively evaluated at Brookhaven National Laboratories as a solidification agent for a number of radioactive wastes including incinerator ash/7/. It can easily be melted and combined with waste components to yield upon cooling a homogeneous solid with compressive strengths significantly higher than those obtained using hydraulic cements. Because no chemical reactions are involved during the solidification, waste constituents do not interfere with the curing of the cement; unlike hydraulic cements, full strength is achieved in hours rather than weeks.

In contrast to the use of solidification binders, interest in managing dispersible wastes such as ash by compaction has been fairly recent/8-11/. This has arisen due to the recent availability of super-compactors for the volume reduction of radioactive waste. Supercompaction of incinerator ash is being practised at Juelich Research Centre - supercompacted ash pellets are placed in overpack drums with the void spaces being filled with concrete. Investigations on potential gas generation/8,10/ in the ash compact due to presence of unoxidised aluminium and iron have indicated the desirability of a pretreatment step involving contact with sodium hydroxide, for instance. In this form the compaction process is similar to the hydrothermal techniques /12-14/ developed by a number of Japanese workers with the principle difference in the latter case being the elevated processing temperature (100-350 deg C) .

Compaction studies are of particular interest because of 1) increased volume reduction due to absence of binders and 2) it is likely that a super-compactor will be acquired and operational within the next 3-5 years. The use of this facility would avoid the necessity of building a separate dedicated facility for conditioning ash.

As in Part 1 of this study, waste forms were assessed based on three NRC stability criteria, namely, compressive strength, leachability and immersion behaviour/15/.

2.0 EXPERIMENTAL

Three types of ash from Bruce were investigated - bottom ash (BA) and baghouse ash (BHA) from the active incinerator and "inactive" ash (IA) from the inactive incinerator. Their characteristics are described in Table 1. The inactive and the baghouse ashes were immobilized "as is" while the BA due to its considerable heterogeneity was screened through a No. 18 screen (1 mm opening).

TABLE 1
CHARACTERISTICS OF BRUCE ASHES/2/

PROPERTY	BOTTOM ASH (BA)	BAGHOUSE ASH (BHA)	INACTIVE ASH (IA)
Size	Very heterogeneous 54 wt % >9.5 mm	Fine and homogeneous 90 wt % <0.8 mm	Similar to BHA 70 wt % <2.4 mm
Bulk Den.	0.68 + 0.27 g/cc	0.34 + 0.08 g/cc	0.29 + 0.11 g/cc
Chemical Composit.	Major elements C, Ca, Fe, Zn, Si and Al C 113 + 45 mg/g	Major elements C, Cl, Zn, Na, S and P C 480 mg/g	Major elem. C,Si, Al, Ca, Ti & Fe C 170 + 93 mg/g
Radiochem. Composit.	2130 + 1320 Bq/g due to Co-60 (28%), La-140 (16%), Zr/Nb-95 (16%) and Cs-134/137 (13%)	2960 Bq/g due principally to Cs-137	

The modified sulfur cement used in this investigation was obtained from Chemical Enterprises, Inc., Houston and is marketed under the tradename Chement 2000. This cement is produced by reacting molten sulfur with 5 wt % mixture consisting of equal parts of the unsaturated hydrocarbon dicyclopentadiene (DCPD) and oligomers of cyclopentadiene (CPD). The material melts at 119 deg C to form a low viscosity liquid. From the standpoint of processing, temperature must be maintained above the melt point but below 159.4 deg. C, the point at which additional polymerization of any residual sulfur occurs causing a sharp increase in viscosity. Immobilized ash samples were prepared by hand blending the ash in the cement melt and transferring the paste into polyethylene containers where they rapidly cooled to form solid waste forms.

Compacted ash samples were produced from wetted ash paste using the equipment shown in Figure 1. The procedure involved the following steps: 1) the bushing with the plug inserted at the bottom was filled with the wet paste, 2) the piston was then introduced into the bushing, 3) the bushing was then mounted below the ram on the hydraulic press and the applied load increased and maintained at 5000 psi (this corresponds roughly to the axial

load in a super-compactor) for 0.5 hr and 4) the sample was finally ejected by removing the slab from below the bushing. When required the band heaters around the bushing were used to heat the sample during Step 3; the outside wall temperature of the bushing was maintained at 250 deg. C during the heating period. Due to difficulties experienced as a result of gas generation in baghouse ash samples, this procedure was applied only to bottom ash samples. Baghouse ash samples following ejection from the bushing were baked for 2 hrs in a muffle furnace maintained at 200 deg. C.

All samples produced had a nominal size of 5 cm diameter * 5 cm height.

Leaching tests using deionized water at room temperature were performed in accordance with the ANS 16.1 static leach test/16/. As required in the test, the ratio of leachant volume to the specimen's geometric surface area (V/S) was maintained at 10 cm. The leachant was completely replaced at 5, 13, 24, 48, 72, 96 and 120 h after initial sample immersion. Solutions were gamma scanned to measure the activity released.

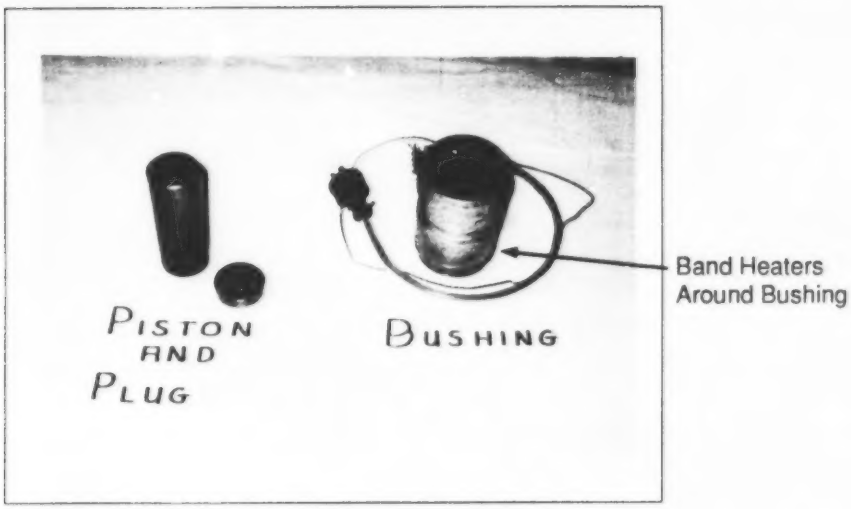
Interpretation of the experimental leaching results was based on diffusional mass transport with an effective diffusivity D defined as:

$$D = \pi \left[\left(\frac{a_n}{A_o}\right) \left(\frac{V}{S}\right) \right]^2 \left[\frac{t - \frac{1}{2}(\Delta t)_n}{(\Delta t)^2_n} \right] \qquad (1)$$

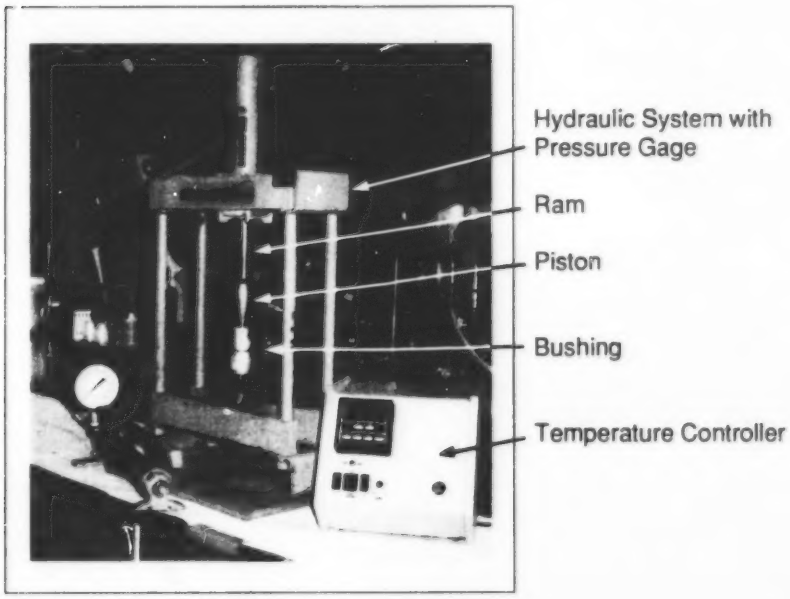
where a_n is the radioactivity of a species released in leaching period n
A_0 is the initial radioactivity of a species in sample
t is the elapsed time
$(\Delta t)_n$ is the duration of a leachant renewal period

An average diffusivity Davg, can be determined from the diffusivity calculated for each leaching period. Logarithm of $1/D_{avg}$ yields the leach index.

Leached samples were immersed in water for an additional duration of 85 days. Following their total immersion period of 90 days, the samples were then compression tested.



(a)



(b)

Figure 1. Equipment Used for Preparing Ash Compacts

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3.0 RESULTS OF SOLIDIFICATION IN SULFUR CEMENT

Preliminary trials were performed to determine the optimal loading of various ashes yielding a visually good product largely free of internal voids and having an acceptable compressive strength (> 60 psi). The low specific heat of sulfur cement can cause an axial void to develop at the centre of the waste form and an assessment of the degree to which this occurred was made using x-ray radiography. The optimal loadings determined for IA, BA, and BHA were 25, 40 and 35 wt. %, respectively (higher loadings can possibly be achieved with better blending equipment). These loadings correspond to 0.53, 0.85 and 0.75 g ash per ml of the waste form, respectively. Compare these values with densities of 0.33, 0.87 and 0.66 g/ml for IA, BA, and BHA, respectively (note these values differ from those reported in Table 1). Thus solidification in sulfur cement results in essentially no volume change for BA while in the cases of IA and BHA there is an overall volume reduction.

Results of compression and leach testing for sulfur cement waste forms are shown in Table 2. Tests were conducted in triplicate. They indicate the following:

TABLE 2
RESULTS OBTAINED FOR SULFUR CEMENT WASTE FORMS

Sample	Compress. Strength (Psi)		Cs-134/137 Leach Index	Heavy Metal Release (ppb)*	
	Before Immersion	After Immersion		5h Leachate	120h Leachate
BA	1330 + 285	2220 + 785	12.5	Cd < 0.2	Cd < 0.4
BHA	1260 + 400	1420 + 730	8.6	Cd 1000	Cd 760
IA	995 + 390	-	-	-	-

* Ag and Pb were not detectable; detection limits 0.2 and 5 ppb respectively.
- Not measured

1) Compressive strengths were significantly higher than the requirement of 60 psi according to 10 CFR Part 61/15/. The type of ash did not appear to influence the compressive strength. The lower strength of IA samples is consistent with their lower ash loading (note that the compressive strength of sulfur cement with no ash loading is lower than with ash loading/7/). The compressive strengths following water immersion either remained unchanged or increased.

2) The only isotopes observed in the leachates were Cs-134 and Cs-137. As expected, their leaching behaviours were essentially identical. For both bottom and baghouse ash samples, the measured leach indices were significantly higher than the requirement of

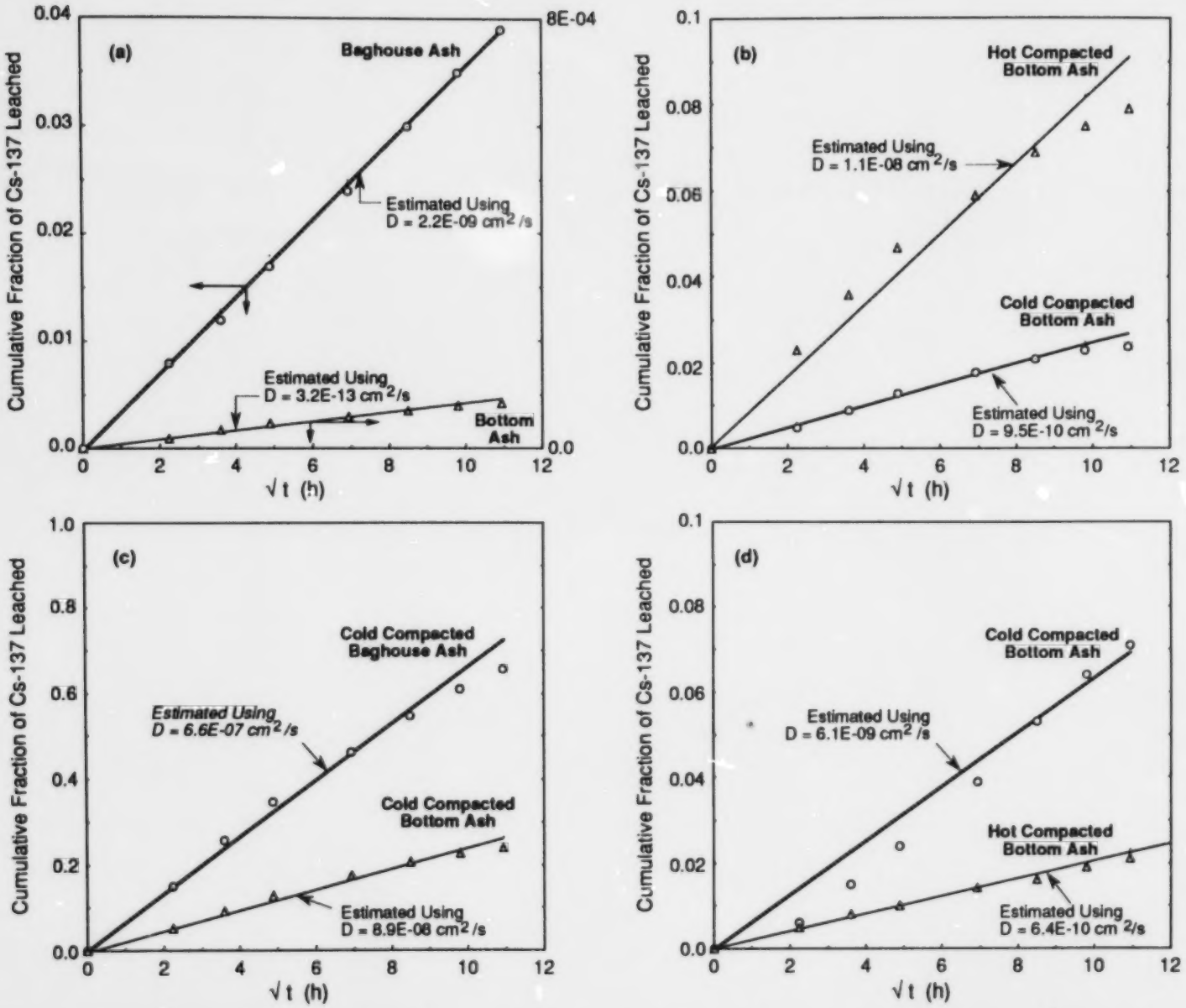

Figure 2. Leach Data for Cs-137 (a) Sulfur Cement Matrix (b) Water Wetted Compact (c) Sodium Hydroxide Wetted Compact (d) Sodium Silicate Wetted Compact

6 according to 10 CFR Part 61/15/. However, the effective diffusivity of the Cs isotopes in the BHA waste forms was orders of magnitude higher than in BA waste forms. As shown in Figure 2, this results in a higher release of Cs-134/137 into the leachant in the case of BHA samples.

Note that the abscissa ($\sqrt{t}$) in Figure 2 was selected in accordance with Equation (2)

$$\frac{\Sigma a_n}{A_o} = \sqrt{\left[\frac{4Dt}{\pi}\left(\frac{S}{V}\right)^2\right]} \qquad (2)$$

for the diffusional release from a semi-infinite medium (the equation is an alternate form of Equation (1) /16/). Also shown in the figure are the estimated (using the measured average diffusivity) releases according to Equation (2); the agreement is excellent.

3) BA and BHA leachates had undetectable concentrations of silver and lead. While the cadmium concentration was barely detectable in the BA leachates, it exceeded the Regulation 309 release limit of 500 ppb in the case of BHA leachates.

4.0 COMPACTION OF ASH

As stated earlier, Ontario Hydro plans to acquire a supercompactor in the near future. Compressive loads which can be applied using such equipment are typically in the order of a few thousand psi. The hydraulic press shown in Figure 1 can be used to apply loads up to 6000 psi and was considered adequate to simulate the ash behaviour during super-compaction. Compaction of dry as well as wetted ash was investigated.

4.1 COMPACTION OF DRY ASH

Figure 3 shows the behaviour of various ashes during compaction. The measurements were performed using a flat bottomed polyethylene insert placed inside the bushing to prevent dispersion of the ash during sample ejection. The insert was filled with a known quantity of ash and then the piston was lowered in to the insert. The length of the piston protruding above the bushing was noted as a function of increasing load; the data were then expressed as a fraction of the original height of the ash in the insert.

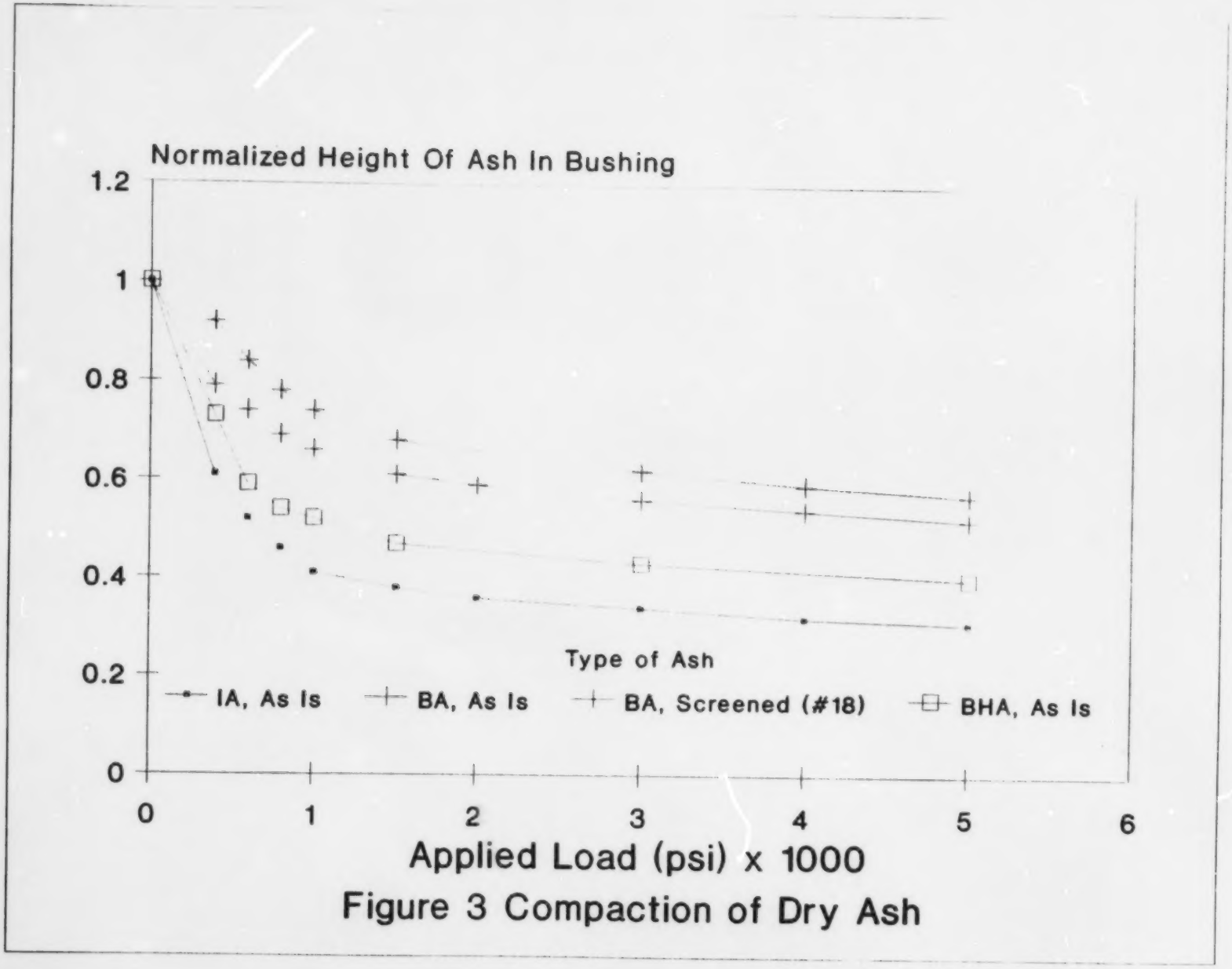

Figure 3 Compaction of Dry Ash

The results indicate that in general the additional volume reduction realized decreased with increasing load. Results for screened (#18 screen) IA and BA ashes (not shown in Figure 3) indicated a similar degree of compaction as the corresponding unscreened ashes. The degree of compaction decreased in the order IA, BHA, BA.

The results are summarised in Table 3. Note the significantly higher density of the compacts compared with the ash densities obtained in sulfur cement or in the other matrices previously investigated.

The ash compacts appeared to be reasonably cohesive. However, they invariably disintegrated during water immersion.

TABLE 3
RESULTS OF DRY COMPACTION

	Density of Ash (g/ml)		
Type of Ash	Before Compac.	After Compac.	Overall VR* at 5000 psi
IA (as is)	0.33	1.06	3.2
IA (screened)	0.31	1.04	3.3
BA (as is)	0.86	1.66	1.9
BA (screened)	0.88	1.54	1.8
BHA	0.66	1.64	2.5

* Volume Reduction

4.2 COMPACTION OF WET ASH

Compaction of wet ash was assessed to improve the density and compressive strength of ash compacts. Three wetting agents were investigated, namely, water, 8N sodium hydroxide solution and sodium silicate[1] solution. Note that in each case, gas generation to some extent (due to reaction of Al and Fe in the ash with the wetting agent) would have occurred prior to compaction. Ash compacts were produced by applying pressure and temperature as previously described.

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[1] Soluble silicates are widely used for pelletizing, granulating and abriquetting of finely divided solids/17/. The solutions contain varying amounts of monomeric silicate ions, polysilicate ions and colloidal silica ion micelles.

The density and pH of the sodium silicate solution used was 1.41 g/mL and 12.2, respectively. The solution contains 9.2 wt% Na_2O and 29.6 wt% SiO_2 (wt. ratio of 3.22) and has a viscosity of about 0.5 poise at 20 °C. For ease of processing, this solution was diluted with equal parts of water before use.

Results of wet compaction studies are summarised in Table 4 and Figure 2. These indicate the following:

1) Compaction of BA using water, sodium silicate or sodium hydroxide yielded products with essentially similar pre-immersion compressive strengths; however, following the 90 day immersion, the compressive strengths of sodium hydroxide wetted ash compacts decreased substantially unlike in the other cases. Further, of three samples prepared using sodium hyroxide, only one sample survived the post-leach immersion period. Application of heat during compaction of water and sodium silicate wetted ash improved the pre-immersion compressive strength but led to sample failure during immersion in the former case. Samples of sodium hydroxide wetted ash with applied heat could not be prepared for testing due to difficulties in sample ejection.

2) The leach index of Cs 134/137 significantly exceeded the 10 CFR Part 61 requirement in all tested BA samples. The leach index improved significantly due to application of heat during the preparation of sodium silicate wetted ash waste forms. Co-60 was not detected in the leachate.

   The leaching behaviour of Cs-137 is shown in Figure 2 (b)-(d). Despite a leach index exceeding 6, the releases of Cs-137 from sodium hydroxide wetted BA and particularly BHA are high. Agreement between measurements and theoretical predictions are not as good as in the case of sulphur cement.

3) The leachate from BA compacts in all cases had heavy metal concentrations at levels significantly lower than Regulation 309 release limits (500 ppb for cadmium and 5000 ppb each for lead and silver). For sodium silicate wetted ash compacts, the heavy metal releases decreased even further when heat was applied during waste form preparation.

4) The general experience with BHA was less satisfactory than with BA. Samples invariably failed during leaching or immersion; Hence, the leach index of Cs 134/137 and heavy metal release could not be assessed in the same manner as for BA samples. No data is reported for sodium silicate wetted BHA because of difficulty in wetting the ash with sodium silicate.

   Heating the ejected samples in the muffle furnace was detrimental to the pre-immersion compressive strength of water wetted BHA. In the case of sodium hydroxide wetted ash, extensive sample disintegration was experienced during heating.

TABLE 4
RESULTS OBTAINED FOR WET COMPACTED WASTE FORMS

Sample	Ash Loading g/ml	Compress.Strength (Psi) Before Immersion	After Immersion	Cs-134/137 Leach Index	Heavy Metal Release (ppb)* Cadmium	Lead	Silver
Ash Wetted with Water							
BA	1.66	220 ± 2	340 ± 50	9.0	10 [1.4]	6 [8]	0.7 [<0.2]
	(1.7)	(335 ± 40)	a	8.0	-	-	-
BHA	2.0	315 ± 165	a	-	-	-	-
	(2.0)	(185 ± 25)	a	-	-	-	-
Ash Wetted with Sodium Silicate Solution							
BA	1.5	355 ± 15	285 ± 40	8.2	6 [nd]	385 [nd]	2.6 [nd]
	(1.5)	(415 ± 100)	(367 ± 0)	(9.3)	(0.9 [1.2]	9 [nd]	nd [nd])
Ash Wetted with 8N Sodium Hydroxide Solution							
BA	1.6	284 ± 2	140	7.1	0.5 [nd]	170 [47]	1.5 [nd]
BHA	1.7	290 ± 9	55	6.2	6800 [2200]	170 [7]	68 [28]

nd Not detectable
a samples failed during leaching period or subsequently during extended immersion.
( ) Data corresponding to application of heat during sample preparation.
* Measured concentrations in 5h (un bracketted) and in 120h (bracketted []) leachate.
Detection limits for cadmium, lead and silver were 0.2, 5 and 0.2 ppb, respectively.

5) Ash loading or density of the wetted ash compacts was similar in the case of BA and somewhat higher in the case of BHA than that obtained by dry compaction.

The overall experience with compaction of sodium hydroxide wetted ash was inconsistent with the success of hydrothermal techniques reported by Japanese workers. While the conditions employed in the present study are less extreme, even under similar conditions the Japanese appear to have better success. Difference in ash composition may partly be responsible. To minimise gas generation in the waste form, the ash was equilibrated with sodium hydroxide for a prolonged duration (1-4 days) prior to compaction. Further, the compacts were allowed to cure for 6 days before being tested. While this approach would likely have reduced the potential of aluminium and iron in the ash to generate hydrogen, the potential of carbon residues particularly in the baghouse ash to form oxidation products at 200 deg. C/2,4/ and thereby cause disintegration of the samples would still exist.

5.0 SUMMARY AND DISCUSSION

The present data along with earlier data on cement, WEP, PE and asphalt are summarised in Table 5. Based on the earlier data, asphalt appeared to be superior to the other matrices for immobilizing both bottom and baghouse ashes. However, the toxicity of cadmium in leachates from asphalted baghouse ash was a concern. While sulfur cement offers some improvement over asphalt with respect to the leach index of Cs-134/137 and the concentration of cadmium in the leachate, the latter still exceeds the Regulation 309 limit of 500 ppb; the gains made are further offset by a significantly lower ash loading in sulfur cement.

In contast to the various solidification matrices, compaction offers sustantially higher ash loadings. Surprisingly, wetted bottom ash compacts have compressive strengths comparable to and leach indices higher than cement (unpelletized) waste forms. Also, the cadmium toxicity in the leachate from the BA compacts does not appear to be a concern. Baghouse ash compacts on the other hand did not have adequate post immersion compressive strength and not surprisingly their leachates contain very high levels of cadmium.

Based on the foregoing and keeping in mind the likelihood of a super-compactor acquisition, the following concept is proposed for managing incinerator ashes:

Mix bottom and baghouse ashes in a drum in the proportion in which they are produ[illegible]16.7 L BA to 1 L BHA in the present incinerator) - this will avoid the nee[illegible] managing BHA separately.

Add a suitable wetting agent and homogenize the contents - the wetting step will minimize the potential for future gas generation and avoid dust arisings during supercompaction.

Supercompact the wetted ash - due to encasement of the ash in a sacrificial metal container during supercompaction, compressive strengths would exceed values measured in this study.

Store compacts in an overpack - the amount of ash in each individual drum being supercompacted will have to be optimized to make effective use of the overpack.

TABLE 5
SUMMARY OF DATA OBTAINED USING VARIOUS MATRICES

Matrix	Ash Loading		Compressive+ Strength (psi)	Cs-137 L.Index	Conc. of Cd (ppb)*
	wt. %	g/ml			
BOTTOM ASH					
Cement[1]	42	0.68	280 (350)	7.3	-
Cement[2]	44	0.71	615 (350)	7.8	-
Cement[3]	51	1.05	3550 (4350)	8.6	nd
WEP	59 (44)	0.89 (0.64)	1650 (4320)	10.3	0.7
PE	40	0.50	-	8.4	< 3
Asphalt	67	1.10	-	11.2	nd
Sulfur C.	40 (25)	0.85 (0.53)	1780 (1000)	12.5	nd
Compact[4]	98	1.66	280	8.9	< 10
Compact[5]	85	1.50	320	8.2	< 6
Compact[6]	76	1.6	210	7.1	< 0.5
BAGHOUSE ASH					
Cement[3]	51	1.05	875	7.0	< 10
PE	40	0.50	-	7.1	> 300
Asphalt	67	1.10	-	7.9	> 1000
Sulfur C.	35	0.75	1350	8.6	880
Compact[4]	> 92	2.0	160	-	-
Compact[5]	77	1.7	175	6.2	4500

1, No plasticizer added; 2, plasticizer added; 3, No plasticizer added, Pelletized; 4, Water wetted ash; 5, Sodium silicate wetted ash; 6, Sodium hydroxide wetted ash; *, corresponding to 5 and 120h leachate; +, Average of pre and post immersion values; nd, Not detectable;

Data in brackets are for inactive ash.

Backfill the space between the compacts and the overpack drum with sulfur cement, asphalt, WEP or cement. Backfilling in the overpack drum will provide an additional barrier to retard the migration of Cs and toxic metal constituents. It will, however, lower the overall volume reduction factor. The ash loading would be reduced from 1.6 g/ml to about 1.4 g/ml (see Appendix).

Reuse the supercompactor liquid effluent thus avoiding the generation of a secondary waste - if the wetting liquid is other than water, make-up chemicals may be required.

Alternately, asphalt appears to be the most suitable solidification matrix based on considerations of ash loading and leachate toxicity (Cs and heavy metals). Unlike sulfur cement, asphalt is available from Canadian sources and has been in use as a solidification matrix at a number of production facilities (e.g. AECL CRNL/18/) for several years now. As in the compaction option, the BHA will need to be blended with BA to minimise cadmium toxicity in the leachate. Unlike compaction, material handling requirements during asphalt/ash blending will probably necessitate screening of the BA and hence separate conditioning of the screened and unscreened ashes.

Note that the BA investigations were made using a relatively fine size fraction of the ash. Coarser particulate is more amenable to compaction than finely divided solids. Therefore, it is probable that properties of compacted waste forms produced from unscreened ash would be at least similar or better than those measured in this study. On the other hand, it is known that the ash characteristics shown in Table 1 are typical only of ash produced since about 1983. Prior to this, the BA generated was less coarse and more uniform due to "as intended" operation of the incinerator; since that time a larger than expected processing load has necesitated a reduction in the residence time causing an adverse effect on the quality of the ash produced. Ash quality is expected to be restored when the present incinerator is replaced.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Among the various options examined, compaction offers the greatest volume reduction for incinerator ashes. Considerations of gas formation in the ash compact and dust generation during processing favour compaction of wetted ash although this does not alter the ash loading for bottom ash as compared with dry compaction. Due to concerns with leachate toxicity, it would be preferable to combine baghouse ash with bottom ash prior to compaction rather than to compact baghouse ashes separately. Further work is required to fully develop the compaction option.

In contrast to compaction, solidification using asphalt yields a lower volume reduction factor. With the expected acquisition of a super-compactor in the near future, there is no incentive

at present to further develop this solidification option. However, should plans for acquiring the supercompactor not materialise or unforseen difficulties arise with implementing ash compaction, asphalt could then be explored further.

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APPENDIX
OVERALL VOLUME REDUCTION FACTOR BY SUPERCOMPACTION

Consider the following/19/:

Volume of sacrificial drum	210 L
Diameter of pellet	62.4 cm
Volume of overpack drum	320 L
Height of overpack drum	96.5 cm
Diameter of overpack drum	65.1 cm

Assume the following:

Fraction of volume or height utilised in sacrificial drum y_1
Fraction of height utilised in overpack drum y_2
Volume reduction (VR) factor for ash by supercompaction 1.6

Then

Volume of compacted ash pellet is 210 y1/1.6 or 131.25 y_1 L
Height of compacted ash pellet is 42.9 y_1 cm
Number of pellets in overpack is $96.5y_2/42.9y_1$ or 2.25 y_2/y_1
Volume of original ash in overpack is 2.25 $y2/y_1$ * $210y_1$ or $472.5y_2$ L
Overall volume reduction factor is $472.5y_2/320$ or $1.48y_2$

Assuming 2 pellets per overpack, $y2/y_1$equals 2/2.25 or 0.89. This limits the maximum value of y_2 to 0.89 corresponding to a value of y_1 of 1. Therefore, overall VR would be less than or equal to 1.32.

If 3 pellets per overpack are assumed then y_2/y_1 equals 1.33. For y_2 to equal 1, y_1 must be 0.75. The overall VR in this case is the maximum it can be, i.e., 1.48. A choice of more than 3 pellets per overpack will also yield an overall VR of 1.48 but will require an unnecessarily greater number of sacrificial drums.

REFERENCES

1. Williamson, A.S., "Radioactive Incinerator Ash Characterization", OHRD Report No. 83-207-K (1983).

2. Krasznai, J.P., "The Characterization of Ash from the BNPD Radioactive Incinerator", OHRD Report No 89-186-K (1989).

3. Krasznai, J.P., "Leachate Toxicity of Radioactive Incinerator Ash", OHRD Report No C90-5-K (1990).

4. Krasznai, J.P. and Husain, A., "Radioactive Incinerator Ash - A Mixed Waste", Proceedings of Second International Seminar on Radioactive Waste Products, Research Centre Julich, Julich, 469-79 (May 28- June 1 '90).

5. US NRC, 10CFR Part 61 - Licensing Requirements for Land Disposal of Radioactive Waste, Final Rule, 47 FR 57473 (December 27, 1982).

6. Husain, A. " Solidification of Radioactive Incinerator Ash - Part 1", OHRD Report No. 90-111-K (1990).

7. Kalb, P.D. and Colombo, P., "Modified Sulfur Cement Solidification of Low Level Wastes", BNL Report No. 51923 (1985).

8. Halaszovich, S., "Uncemented Supercompacted Ash - The Preferential Final Waste Form for Low Level Radioactive Waste", Presented at the Symposium on Waste Management at Tucson, Arizona (1990).

9. Jouan, A. et al, "Incineration Ash Conditioning Processes", Proc. of Incineration Conference, San Diego, California (May 14-18, 1990).

10. Jouan, A. et al, "Conditioning Processes for Incinerator Ashes", Presented at the Technical Seminar on Conditioning of Radioactive Incinerator Ashes at Aix-en-Provence, France (June 12-15, 1990).

11. Laser, M., "Gas Production by Reaction of Water or Alkaline Solutions with LAW Ashes", Presented at the Technical Seminar on Conditioning of Radioactive Incinerator Ashes at Aix-en-Provence, France (June 12-15 1990).

12. Katakura, M. et.al., "Study And Development of Incinerator Ash Immobilization By Hydrothermal Solidification", International Waste Management Conference, Hong Kong, 303-308 (Nov.29 - Dec.5, 1987).

13. Yamasaki, N. et al., "A Hydrothermal Hot Pressing Method: Apparatus and Application", J. Materials Science Letters 5, 355-6 (1986).

14. Yanagisawa, K. et al., "Immobilization of Radioactive Wastes By Hydrothermal Hot Pressing", Am. Ceram. Soc. Bull., 64 (12), 1563-7 (1985).

15. US NRC, "Technical Position on Waste Form", Rev. 0 (May 1983).

16. Neilson, R.M. Jr., "Experimental Procedure for Proposed ANS Standard on Low Level Waste Leachability", Trans. Am. Nucl., Soc. 33, 203 (1979).

17. Weldes, H.H and Lange, K.R., "Properties ot Soluble Silicates", Industrial and Engineering Chemistry, 61(4), 29-44 (April 1969).

18. Buckley, L.P. and Pettipas, W.H., "Bituminization of Reactor Wastes: Development Design and Demonstration", Presented at the Second Annual Meeting of the Canadian Nuclear Soc., Ottawa, Canada (June 1981).

19. Krochmalnek, L.S., Private Communication (March 22, 1991).